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# Petrography, geochemistry and geochronology of igneous rocks from the Jiangnan Orogen, South China: constraints on the Early Paleozoic tectonic evolution of the South China Block

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The Early Paleozoic tectonic evolution of the South China Block (SCB) remains controversial related to intracontinental orogenic and oceanic subduction processes. We present whole-rock major and trace elemental data, LA-ICP-MS zircon U-Pb age and Lu-Hf isotopic data for the Early Paleozoic igneous rocks including granodiorites from the Yuechengling pluton and volcanic breccias from the Damingshan pluton from the western segment of the Jiangnan Orogen in the SCB. LA-ICP-MS zircon U-Pb dating yielded emplacement ages for the Yuechengling S-type granitoids of 438–436 Ma and the deposited age for the Damingshan volcanoclastic rocks to be later than 451 Ma. The Yuechengling granitoids have consistent SiO<sub>2</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>, MgO, and P<sub>2</sub>O<sub>5</sub> contents, higher Al<sub>2</sub>O<sub>3</sub> contents, and Na<sub>2</sub>O + K<sub>2</sub>O values, but lower Mg<sup>#</sup> values, compared with those of the Damingshan volcanoclastic rocks. All the studied samples exhibit enrichment in LREEs and moderate negative Eu anomalies ( $\delta\text{Eu} = 0.63\text{--}0.75$ ), with negative Ba, Sr, Nb, Ta, P, and Ti anomalies, and positive Rb, Th, U, Pb, and K anomalies. The granitoids have variable CaO/Na<sub>2</sub>O ratios of 0.22–1.11, negative  $\epsilon_{\text{Hf}}(t)$  values of  $-11.98$  to  $-0.90$ , and corresponding  $T_{\text{DM2}}$  ages distributed from 2.37 to 1.55 Ga. The petrographic and geochemical characteristics of the Yuechengling granitoids indicate that their parental magma was derived from a crustal meta-greywacke and meta-pelite components in the Paleoproterozoic basement, and have undergone some degree of fractional crystallization. The volcanoclastic rocks have mostly negative  $\epsilon_{\text{Hf}}(t)$  values with partially positive ( $-27.54$  to  $8.73$ ), and zircons with negative  $\epsilon_{\text{Hf}}(t)$  values ( $-27.54$  to  $-0.14$ ) show  $T_{\text{DM2}}$  ages of 3.79 to 1.63 Ga. Combined with petrographic and geochemical data, we suggest that the Damingshan volcanoclastic rocks were derived from Neoproterozoic-Neoproterozoic crustal materials and the felsic parental magma has undergone some degree of magma mixing with mantle material, and deposited soon after a Late Ordovician volcanic eruption (later than 451 Ma). Integrated with previous studies, our new data support the intracontinental orogenic model to account for the Early Paleozoic tectonic evolution. Thus, we suggest that the Early Paleozoic tectonic setting of the SCB was intracontinental orogeny rather than oceanic subduction-collision.

## KEYWORDS

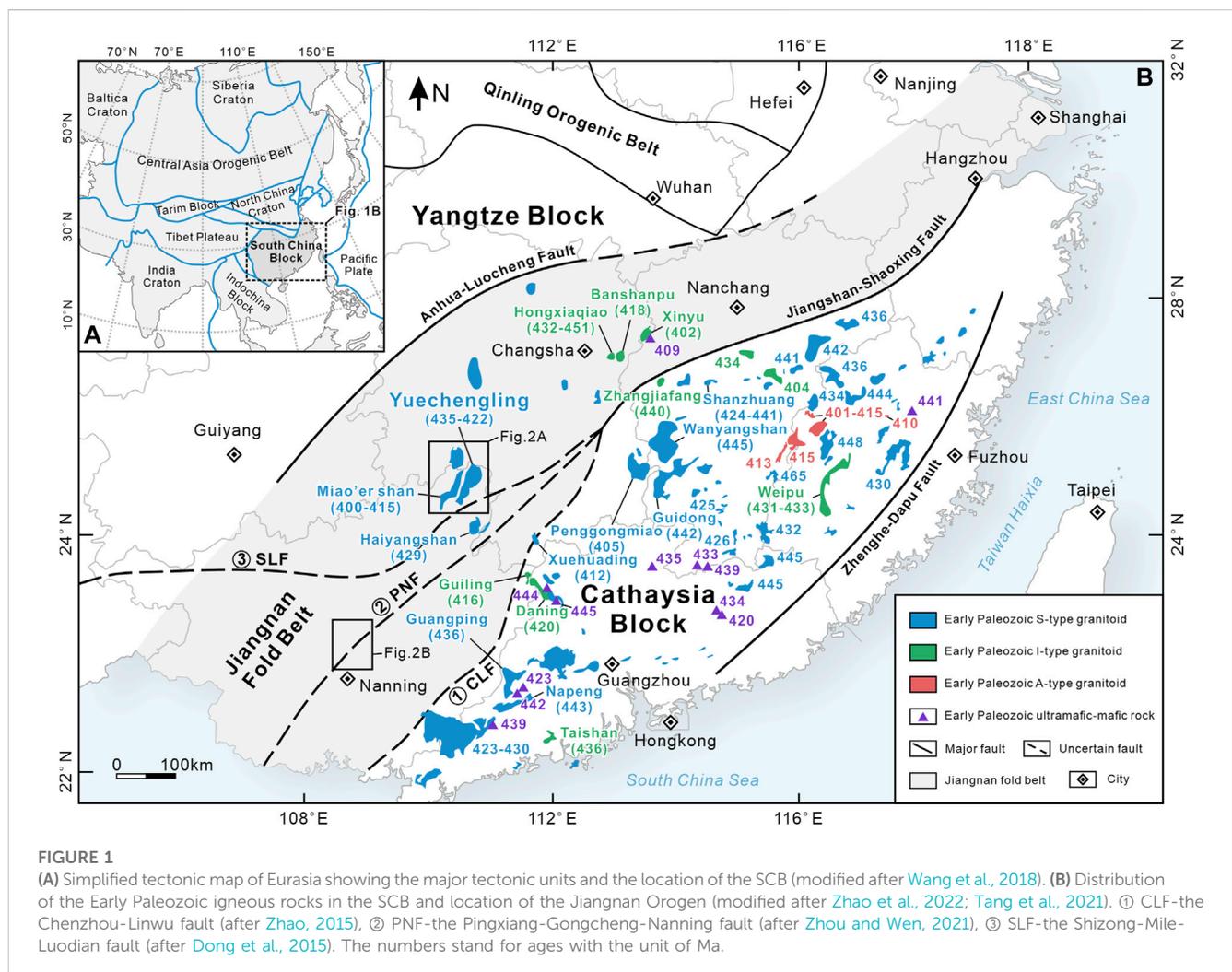
the South China Block, igneous rock, zircon U-Pb geochronology, geochemistry, Hf isotope

## 1 Introduction

The SCB, a major continental block of East Asia, is located in southeast Eurasia and the convergence area of Eurasian and Pacific Plates (Figure 1A). The block consists of the Yangtze Block to the northwest and the Cathaysia Block to the southeast, which were welded together during the Neoproterozoic along the Jiangnan fold belt (the Jiangnan Orogen, Figure 1B) (Charvet, 2013; Yao et al., 2014; Shu et al., 2015). The SCB had undergone three episodes of tectonic evolution of the Proto-(Early Paleozoic), the Paleo-(Late Paleozoic) and the Neo-(Mesozoic-Cenozoic) Tethys since Neoproterozoic, corresponding to three tectonic evolution stages of the Caledonian (Early Paleozoic), Indosinian (Early Mesozoic) and Yanshanian-Himalayan (Late Mesozoic-Cenozoic) (Zhang et al., 2013). As the first extensive tectono-thermal event in the SCB since the Neoproterozoic break-up of the Rodinia supercontinent (Wang et al., 2011; Huang et al., 2013; Yu et al., 2016), the Early Paleozoic orogeny strongly affected the final tectonic framework of the SCB (Shu, 2012; Zhang et al., 2013),

which is characterized by high-grade metamorphism, intensive deformation, wide-spread magmatism and unconformities (Charvet et al., 2010; Liu et al., 2010; Wang et al., 2011; Zhang et al., 2015; Tang et al., 2021).

Despite decades of considerable research, the Early Paleozoic orogeny remains uncertain with regard to its tectonic setting and geodynamic driving force (Charvet et al., 2010; Wang et al., 2010; Huang et al., 2013; Shu et al., 2014; Yu et al., 2016). Two opposing tectonic setting models of oceanic subduction-collision and intracontinental orogeny are proposed, controversy still exists regarding the Early Paleozoic “Huanan Ocean” in the SCB. Some researchers proposed that the Yangtze and Cathaysia Blocks were amalgamated together into the ancient South China continent during the amalgamation process of the Rodinia supercontinent in the Late Neoproterozoic and the Early Paleozoic “Huanan Ocean” did not exist (e.g., Charvet et al., 2010; Huang et al., 2013; Xia et al., 2014; Shu et al., 2015; Tang et al., 2021). While others believed that the “Huanan Ocean” existed in the Early Paleozoic and the oceanic subduction occurred (e.g., Hsü et al., 1990; Qin et al., 2011; Peng



et al., 2016a; Peng et al., 2016b; Liu et al., 2018). Based on the Early Paleozoic ultramafic-mafic rocks (e.g., Yao et al., 2012; Wang et al., 2013b; Zhang et al., 2015) and I-type granitoids (e.g., Huang et al., 2013; Zhang et al., 2015; Yu et al., 2016; Tang et al., 2021), a model of the Early Paleozoic magmatic activity in the SCB was related to the partially molten SCLM (Sub-Continental Lithospheric Mantle) heated by upwelling asthenosphere triggered by lithospheric delamination is proposed. However, there was no consensus concerning the geodynamic framework of the Early Paleozoic orogeny.

The Jiangnan Orogen is located in the southeastern margin of the Yangtze Block and is bound on its southeastern side by the Cathaysia Block along the Jiangshan-Shaoxing fault as the eastern boundary, with a width of ca. 120 km and length of ca. 1,500 km (Figure 1B; Wang X. L. et al., 2007; Yao et al., 2014), which could be divided into the eastern and western segments by the border of Hunan and Jiangxi provinces. Due to poor exposure and thermo-tectonic modification (Li et al., 2010; Shu, 2012), the southwestern boundary of the western segment is unclear and several faults have been proposed, such as the Pingxiang-Gongcheng-Nanning fault (e.g., Zhou and Wen, 2021), the Chenzhou-Linwu fault (e.g., Zhao, 2015), and the Shizong-Mile-Luodian fault (e.g., Dong et al., 2015). The Jiangnan Orogen is considered to represent the subductional-collisional suture between the Yangtze and Cathaysia Blocks (Yao et al., 2014), which is a key to understanding the assembly and evolution of the SCB (Wang X. L. et al., 2007; Lin et al., 2008; Charvet et al., 2010; Zhao et al., 2016). Therefore, the temporal-spatial pattern and petrogenesis of the Early Paleozoic igneous rocks in the western segment can provide particular constraints on the tectonic setting and evolution of the Early Paleozoic orogeny (Wang et al., 2010; Wang et al., 2013a; Zhong et al., 2013; Shu et al., 2014; Shu et al., 2015). Moreover, previous studies are mostly focused on the granitoids in the SCB (e.g., Huang et al., 2013; Zhao et al., 2013; Zhong et al., 2013; Yu et al., 2016; Cai et al., 2017; Xin et al., 2020; Tang et al., 2021), while less attention has been paid on the Early Paleozoic volcanic-volcaniclastic rocks. Consequently, we studied the Early Paleozoic intrusive and extrusive rocks located in northeastern and central Guangxi province in the western segment, which are of great significance for constraining the Early Paleozoic magmatism, tectonic evolution, and geodynamic driving force of the SCB. Based on field geological investigation, we present new zircon U-Pb ages, Hf isotopic compositions, and whole-rock geochemical data for the Early Paleozoic igneous rocks to reveal their petrogenesis, and further offer new perspectives on the Early Paleozoic tectonic setting of the SCB.

## 2 Geological setting and sample descriptions

The Yangtze and Cathaysia Blocks were amalgamated and separated in multiple tectonic evolutions from the Mesoproterozoic to Neoproterozoic (Charvet et al., 1996; Wang et al., 2011; Shu, 2012; Shu et al., 2014; Shu et al., 2015). The basement of the Yangtze Block is Archean tonalitic-trondhjemitic-granodioritic (TTG) gneisses with ages of 3.2–2.9 Ga in the north (e.g., the Kongling Group) and Paleoproterozoic strata in the west (e.g., the Hekou Group), overlain by a Neoproterozoic to Cenozoic

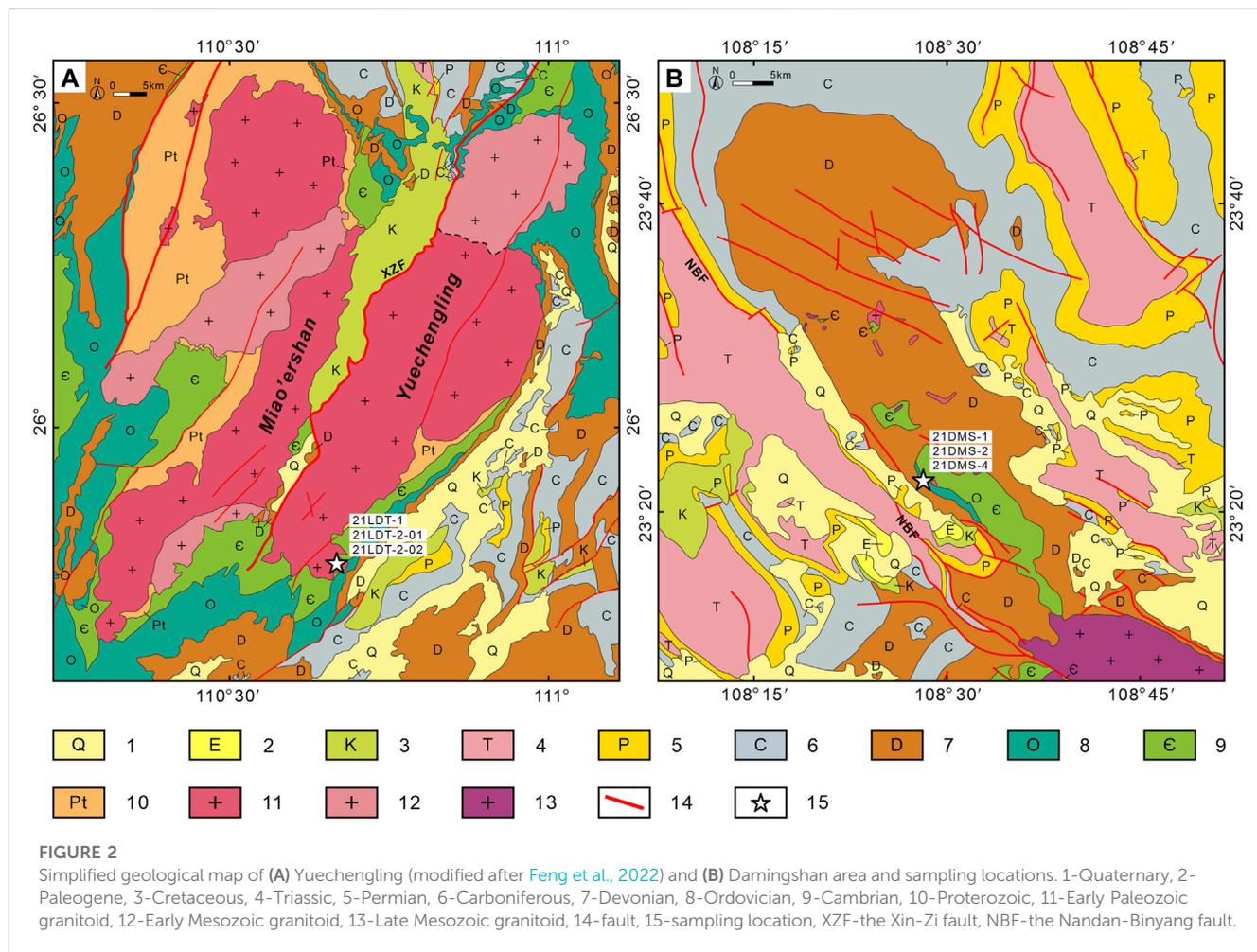
cover (Qiu et al., 2000; Jiao et al., 2009; Wang et al., 2013b; Tang et al., 2021). The basement of the Cathaysia Block has a Paleoproterozoic origin (1.8–2.0 Ga), which is dominantly composed of schist, gneiss, amphibolite, migmatite and volcanoclastics (Liu et al., 2009; Yu et al., 2009; Yu et al., 2010; Wang et al., 2013b), while the Jiangnan Orogen consists mostly of the Paleoproterozoic to Early Neoproterozoic sedimentary strata and igneous rocks (Wang et al., 2008; Shu et al., 2015; Zhao et al., 2022).

Most of the Early Paleozoic igneous rocks in the SCB are distributed in southeastern margin of the Yangtze Block (the Jiangnan Orogen) and northwestern-western margin of the Cathaysia Block (Figure 1B). Recently, the increasing discovery of S-type (e.g., Wang et al., 2011; Zhang et al., 2012; Shu et al., 2015), I-type (e.g., Huang et al., 2013; Zhong et al., 2013; Zhang et al., 2015; Yu et al., 2016; Tang et al., 2021), and A-type (Feng et al., 2014; Cai et al., 2017; Xin et al., 2020) granitoids, ultramafic-mafic (Wang et al., 2013b; Zhong et al., 2013; Zhong et al., 2014; Zhong et al., 2016; Zhang et al., 2015), and intermediate (Zhong et al., 2016) intrusive rocks, volcanic rocks (Yao et al., 2012; Zhang X. S. et al., 2017; Qin et al., 2017; Liu et al., 2018), and metamorphic rocks (Wang Y. J. et al., 2007; Li et al., 2011) from the SCB have been reported. Geochronological studies indicate that the magmatism in the Early Paleozoic initiated in the Late Ordovician (ca. 460 Ma) and lasted until the Late Devonian (ca. 390 Ma) (Li et al., 2011; Wang et al., 2013b; Xin et al., 2020; Kong et al., 2021; Tang et al., 2021 and the related references).

In this study, granitoids from the Yuechengling pluton and volcanoclastic rocks from the Damingshan pluton located in the western segment of the Jiangnan Orogen were studied (Figure 1B), aiming to constrain the petrogenesis of the igneous rocks and offer new perspectives on the tectonic-thermal evolution and tectonic setting of the Early Paleozoic magmatic activity in the SCB. The sampling locations and mineral compositions of the samples are shown in Figure 2 and Table 1.

### 2.1 The Yuechengling pluton

The Yuechengling pluton is located in the border region of Guangxi and Hunan Provinces, which is mainly composed of the Early Paleozoic granitoids with a surface area of more than 3,000 km<sup>2</sup> (Wu et al., 2012; Chen et al., 2016). It showed a NEE-trending distribution with the outcropped strata of Proterozoic (Pt), Cambrian (Є), Ordovician (O), Devonian (D), Carboniferous (C), Permian (P), Cretaceous (K), and Quaternary (Q) (Figure 2A). There are two episodes of granitic magmatic activities and the Early Paleozoic (435–422 Ma) granite (Zhao et al., 2013; Bai et al., 2015; Chen et al., 2016 and the related references) in the south and associated Early Mesozoic (236–222 Ma) granite (Chu et al., 2012; Feng et al., 2022 and the related references) in the north were produced respectively. Many deposits of W-Sn-Mo-Pb-Zn-Cu are surrounding the contact zone between the pluton and strata, forming an ore-rich belt around the Yuechengling pluton (Wu et al., 2012; Chen et al., 2016). Many scholars have constrained the geochronological, lithological, geochemical, petrogenesis (e.g., Zhao et al., 2013; Bai et al., 2015; Chen et al., 2016) and mineralization of non-ferrous metals (e.g., Chen et al., 2016;

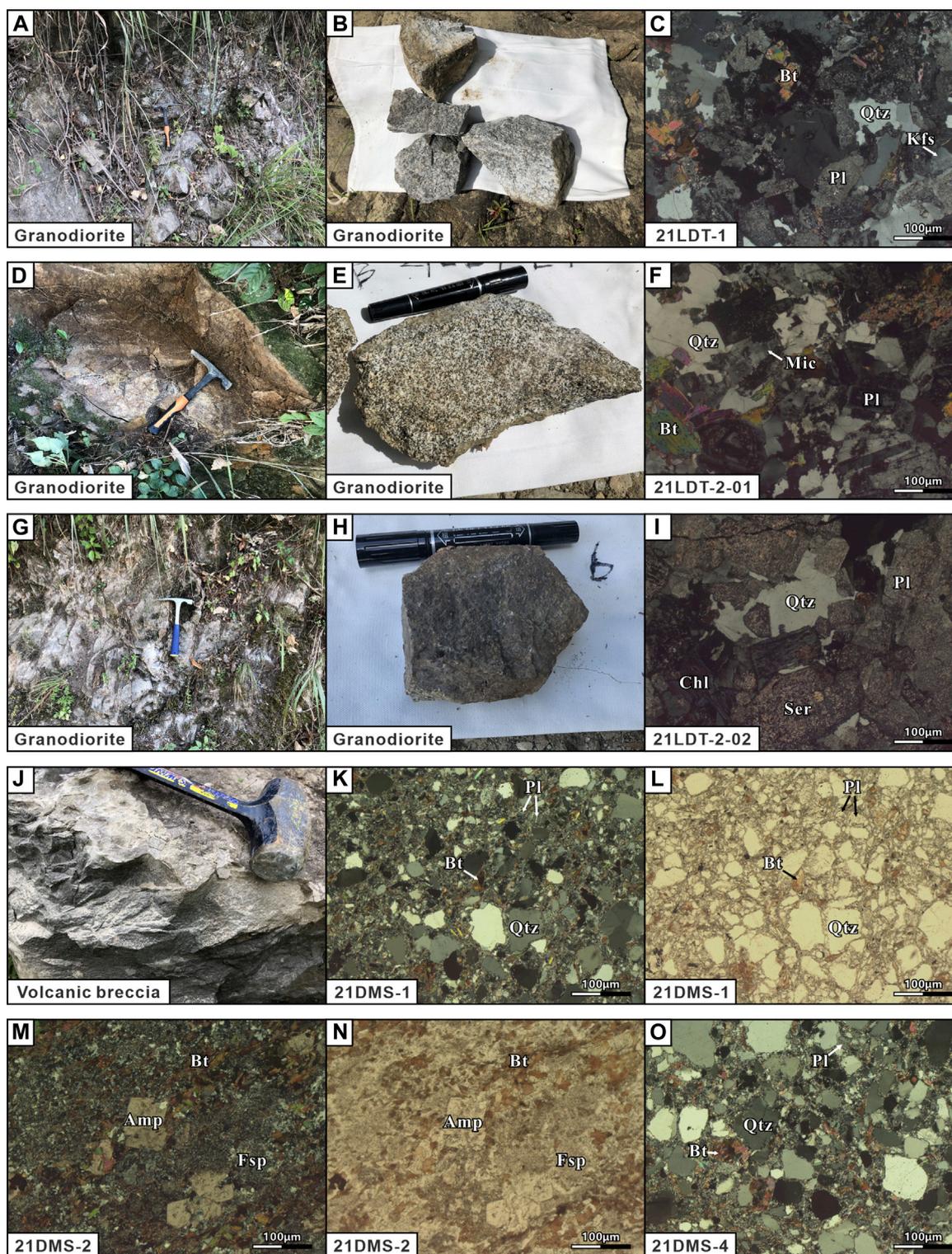


**TABLE 1** The sampling location, lithology and mineral assemblages of the Yuechengling granitoids and the Damingshan volcanoclastic rocks.

Pluton	Sample NO.	Lithology	Location	Mineralogy
Yuechengling	21LDT-1	granodiorite	N25°47'4.6", E110°40'42.3"	quartz (50%) + plagioclase (40%) + K-feldspar (5%) + biotite (5%)
	21LDT-2-01	granodiorite	N25°47'16.2", E110°40'37.2"	quartz (40%) + plagioclase (20%) + K-feldspar (20%) + biotite (20%)
	21LDT-2-02	granodiorite	N25°47'14.4", E110°40'37.3"	quartz (45%) + K-feldspar (30%) + plagioclase (15%–20%) + biotite (5%–10%)
Damingshan	21DMS-1	volcanic breccia	N23°23'04", E108°28'01"	detritus (60%): quartz (70%) + plagioclase (20%) + biotite (10%); matrix (40%): quartz + sericite
	21DMS-2	volcanic breccia		detritus (50%): quartz (50%) + biotite (10%) + calcite (20%) + feldspar (20%); matrix (50%): quartz + calcite + sericite
	21DMS-4	volcanic breccia		detritus (70%): quartz (90%) + feldspar (5%) + muscovite (5%) + detritus (<1%); matrix (30%): quartz + sericite

Zhang W. L. et al., 2017; Chen et al., 2018) for the Early Paleozoic and Early Mesozoic granites in the study area. Despite numerous studies are available, disputes still exist and further work is needed to refine the tectono-thermal evolution and tectonic setting.

The granodiorite samples (21LDT-1, 21LDT-2-01, and 21LDT-2-02) were collected from south of the Yuechengling pluton (Figure 2A), which have typical granitic textures (Figure 3). These rocks consist mainly



**FIGURE 3**

Field, Hand specimen and microscopic photographs of the Yuechengling granitoids (A–I) and the Damingshan volcaniclastic rocks (J–O). Abbreviations: Qtz-quartz, Pl-plagioclase, Kfs-K-feldspar, Bt-biotite, Mic-microcline, Chl-chlorite, Ser-sericite, Amp-amphibole, Fsp-feldspar.

of quartz, plagioclase, K-feldspar, and biotite, while the accessory minerals are mainly magnetite and apatite (Figure 3; Table 1). They have experienced variable degrees of

alteration, and exhibit kaolinization and chloritization of K-feldspar and biotite, and sericitization of plagioclase, respectively (Figure 3).

## 2.2 The Damingshan pluton

The Damingshan pluton is located in the southeastern margin of Youjiang rift basin, central Guangxi Province. The NW-SE trending Nandan-Binyang fault is the main fault, which passes across the Damingshan composite anticline from northwest to southeast. The strata outcropped are from Cambrian (Є) to Quaternary (Q), with Silurian (S) and Jurassic (J) are missing (Figure 2B). Ordovician distributed in the southwest of the Damingshan anticline in an NW-trending strip (Figure 2B), with lithology of greywacke, shale, mudstone, pyroclastic rock, etc., and shows parallel unconformity with the underlying Cambrian strata and angular unconformity with the overlying Devonian strata. Ordovician only outcropped at the Huang'ai formation (O1h), which distributed in Longtoushan, Shanglin County. Previous studies for the Damingshan pluton mainly focused on deposits (Cai, 2012; Gan et al., 2022) by using geochronology (Yang et al., 2011) or geochemistry (Zhou, 2020) methods, only a few systematic chronology and geochemistry studies had been conducted on the igneous rocks (Chen, 2018; Wang et al., 2020).

The volcanoclastic samples (21DMS-1, 21DMS-2, and 21DMS-4) were collected from the Ordovician strata. The detritus consists of quartz, feldspar, calcite, biotite, and muscovite, most of the quartz and feldspar minerals have been sericitized (Table 1; Figure 3). The component of the matrix is mainly quartz and sericite, with calcite only appearing in sample 21DMS-2 (Table 1; Figure 3).

## 3 Analytical methods

Whole-rock major and trace element compositions were determined for the granitoid and volcanoclastic samples. The zircons from these samples were used for laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS) zircon U-Pb dating and multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) zircon Lu-Hf isotope analyses.

Major and trace element compositions were undertaken at Guangxi Key Laboratory of Exploration for Hidden Metallic ore Deposits, Guilin University of Technology. Major element compositions were determined using a ZSX Primus II X-ray fluorescence spectrometer (XRF) and the analytical accuracy was better than 2%. Trace element compositions were determined using an Agilent 7500cx inductively coupled plasma mass spectrometry (ICP-MS) and the analytical accuracy was better than 2%. The analytical procedures have been described by Liu X. J. et al. (2020).

Zircon U-Pb dating and Hf isotope analyses were performed at Guangxi Key Laboratory of Hidden Metal Mineral Exploration at Guilin University of Technology. The instrument used for the zircon U-Pb dating was LA-ICP-MS, with a laser beam spot diameter of 32  $\mu\text{m}$  and a frequency of 6 Hz. To ensure reliability of the analyses and stability of the instruments, standard samples were analyzed before and after each group of analyses, using the American national standard silicate glass NIST610. The external standard 91,500 was analyzed twice before and after each group of eight analyses, and internal standard samples were limited by GJ. The measured data were processed using ICPMSDataCal10.2 software, and the U-Pb harmonic graphs and age-weighted average graphs of

samples were drawn using Isoplot v4.15. The zircon *in situ* Hf isotope analyses were performed using a high-resolution multi-receiver ICP-MS system equipped with an ESI New Wave 193 Ar F excimer laser. The methods were described by Bouvier et al. (2008). Standard zircon GJ whose  $^{176}\text{Hf}/^{177}\text{Hf}$  value is  $= 0.282000 \pm 50$  ( $2\sigma$ ) was used for external correction, initial  $^{176}\text{Hf}/^{177}\text{Hf}$  values calculations were based on Lu decay constant of  $1.865 \times 10^{-11} \text{ yr}^{-1}$  (Scherer et al., 2001). Model ages and  $\varepsilon_{\text{Hf}}(t)$  values were calculated under the supposition that the  $^{176}\text{Lu}/^{177}\text{Hf}$  of average crust is 0.015, the  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios of chondrite are 0.282772 and 0.0332, and ratios of depleted mantle at the present are 0.28325 and 0.0384, respectively (Blichert Toft and Albarède, 1997; Griffin et al., 2004).

## 4 Analytical results

### 4.1 Zircon characteristics and U-Pb dating results

#### 4.1.1 The Yuechengling granitoids

Zircon U-Pb ages were obtained and shown in Supplementary Table S1. Zircon grains of sample 21LDT-1, 21LDT-2-01, and 21LDT-2-02 are mostly shaped in prismatic and euhedral, only a few are irregular anhedral and ellipse shapes, mostly 80–210  $\mu\text{m}$  long and 40–80  $\mu\text{m}$  wide, with length/width ratios of 1:1–4:1. As shown in the cathode luminescence (CL) images (Figures 4A–C), most of the zircon grains display a clear oscillatory zonation, which is typical of magmatic origin zircons.

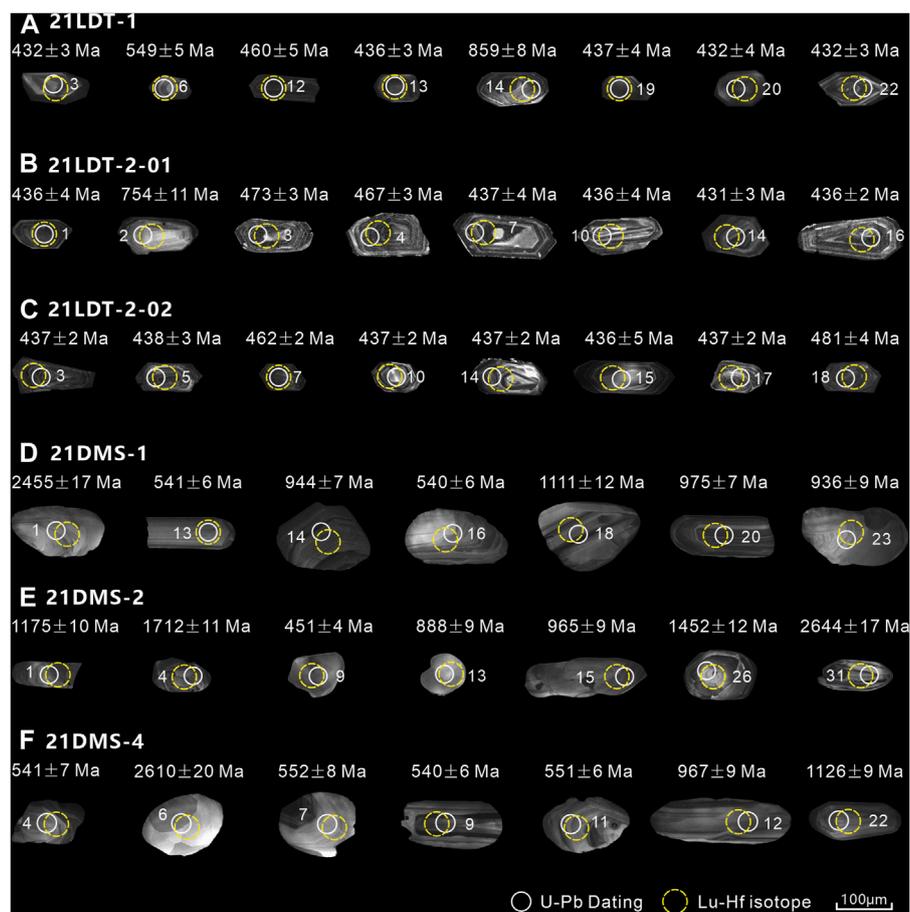
Twenty-two spot analyses were conducted in sample 21LDT-1 (granodiorite) and the CL images show that most of the zircons have magmatic oscillatory zonation (Figure 4A). 22 zircon grains exhibit Th/U values of  $> 0.2$  and 18 of them display age data with  $\geq 90\%$  concordance, giving a weighted mean age of  $437.0 \pm 2.7 \text{ Ma}$  (MSWD = 2.9, Figure 5A). The remaining four concordant grains show older  $^{206}\text{Pb}/^{238}\text{U}$  age of 859–549 Ma (Supplementary Table S1), which are probably inherited or captured zircons.

A total of 17 analyses in sample 21LDT-2-01 (granodiorite) exhibit well-developed magmatic oscillatory zonation (Figure 4B) and show concordant ages with  $\geq 90\%$  concordance and Th/U values of  $> 0.2$ . Five zircon grains have consistent  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 475 Ma to 467 Ma (Supplementary Table S1), with a weighted mean age of  $470.7 \pm 2.9 \text{ Ma}$  (MSWD = 0.62, Figure 5B). 11 zircon grains have younger ages ranging from 431 Ma to 440 Ma, with a weighted mean age of  $436.0 \pm 1.8 \text{ Ma}$  (MSWD = 0.55, Figure 5B). The remaining one inherited zircon grains was formed in Neoproterozoic (754 Ma).

Zircons from sample 21LDT-2-02 (granodiorite) exhibit magmatic oscillatory zonation in CL images (Figure 4C) and Th/U values of  $> 0.2$ . 20 zircon grains show concordant ages with  $\geq 90\%$  concordance and 16 of them have consistent  $^{206}\text{Pb}/^{238}\text{U}$  ages ranging from 445 Ma to 436 Ma (Supplementary Table S1), with a weighted mean age of  $437.8 \pm 1.4 \text{ Ma}$  (MSWD = 0.92, Figure 5C). The remaining four zircon grains show older age of 481–462 Ma.

#### 4.1.2 The Damingshan volcanoclastic rocks

Zircon grains in sample 21DMS-1, 21DMS-2, and 21DMS-4 are mostly shaped in irregular anhedral and round-ellipse in shapes. They feature in size of 50–320  $\mu\text{m}$  long and 45–160  $\mu\text{m}$  wide, with



**FIGURE 4**  
Cathode luminescence (CL) images of zircons from the Yuechengling granitoids (A–C) and the Damingshan volcaniclastic rocks (D–F).

length/width ratios of 1:1–4:1. As shown in the CL images (Figures 4D–F), most of the zircon grains display a clear oscillatory zonation, which is typical of magmatic origin zircons.

A total of 31 analyses were conducted on zircon grains from sample 21DMS-1 (volcanic breccia), and all have concordant ages with  $\geq 90\%$  concordance and Th/U values of  $> 0.2$ , defining an age range from 2,478 Ma to 521 Ma (Supplementary Table S1; Figure 5D). These grains define two detrital zircon age modes at ca. 970 Ma and 540 Ma. The oldest zircon grains have an Early Paleoproterozoic age (2,478 Ma) and some detrital zircons define Mesoproterozoic–Neoproterozoic ages (1703–645 Ma). Eight zircons were formed in the Early Paleozoic (542–521 Ma) with the youngest age of  $521 \pm 6$  Ma (96% concordance), which is interpreted to be a maximum depositional age of the rock.

Almost all the 31 zircons in the 21DMS-2 (volcanic breccia) define concordant ages with  $\geq 90\%$  concordance. The high Th/U ratios suggest most of magmatic origin. The zircon grains show a wide age range spanning from 2,644 Ma to 451 Ma (Supplementary Table S1; Figure 5E), with a major Neoproterozoic peak ( $\sim 970$  Ma) and minor Early Paleozoic peak ( $\sim 530$  Ma). Three young zircon grains yield Early Paleozoic ages from 543 Ma to 451 Ma, the youngest age of  $451 \pm 4$  Ma (98% concordance) constraining the timing of deposition to be later than 451 Ma.

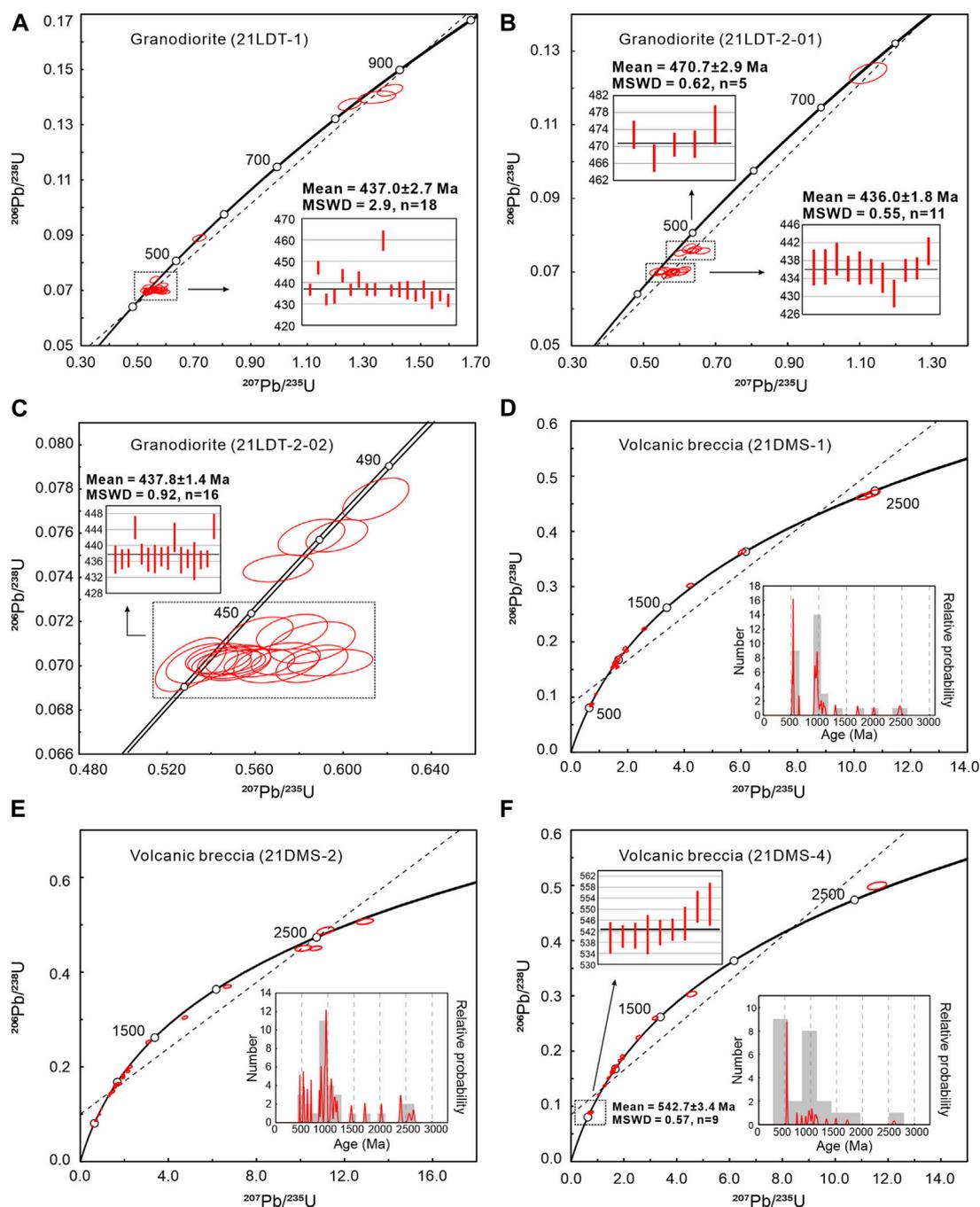
All of the 24 zircon grains in sample 21DMS-4 (volcanic breccia) show concordant ages with  $\geq 90\%$  concordance. The zircon grains also define a broad age ranging from 2,610 Ma to 540 Ma (Supplementary Table S1; Figure 5F) with a peak at  $\sim 970$  Ma and also carry an Early Paleozoic peak at  $\sim 540$  Ma. Nine youngest concordant zircons show ages of Early Paleozoic between 552 Ma and 540 Ma with a weighted mean age of  $542.7 \pm 3.4$  Ma (MSWD = 0.57, Figure 5F), suggesting the maximum depositional age.

## 4.2 Whole-rock major and trace elements

### 4.2.1 Major elements

Whole-rock major and trace element compositions are presented in Supplementary Table S2.

Granitoids from the Yuechengling pluton have  $\text{SiO}_2$  contents of 66.12–67.32 wt%, low  $\text{Fe}_2\text{O}_3^{\text{T}} + \text{MgO}$  contents of 5.98–6.31 wt% and  $\text{Mg}^{\#}$  values [ $\text{Mg}^{\#} = \text{atomic Mg}/(\text{Mg} + \text{Fe})$ ] of 48–49,  $\text{TiO}_2$  of 0.45–0.48 wt%,  $\text{P}_2\text{O}_5$  of 0.11–0.13 wt% and high  $\text{Al}_2\text{O}_3$  contents of 14.97–16.30 wt%. They have total alkali (ALK =  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) values of 6.10–6.59 wt% and A/CNK [A/CNK = molar  $\text{Al}_2\text{O}_3/(\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$ ] values of 1.18–1.55 with strongly peraluminous characteristics and plot in the granodiorite and high-K calc-alkaline



**FIGURE 5**  
 Concordant zircon U-Pb dating diagrams of igneous rocks from the Yuechengling pluton (A–C) and the Damingshan pluton (D–F).

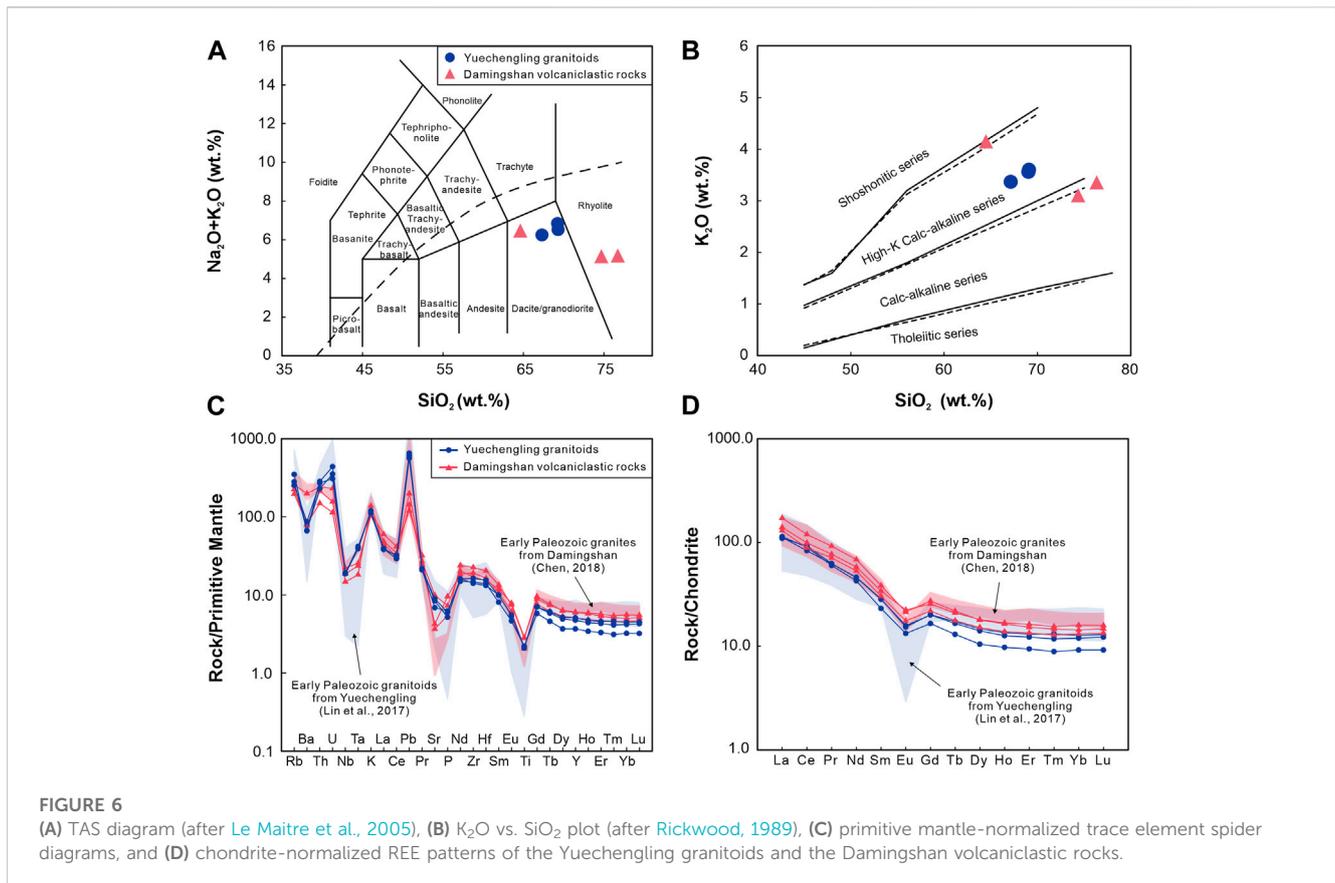
series fields in the total alkali vs. alkali (TAS) and  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$  diagrams (Figures 6A, B). Most of the samples have loss on ignition (L.O.I.) values of <2.5 wt% (1.02–2.44 wt%), indicating weak weathering or secondary alteration.

In contrast, volcanoclastic rocks from the Damingshan pluton have variable  $\text{SiO}_2$  contents of 61.23–74.07 wt%, CaO of 0.74–2.91 wt%,  $\text{Fe}_2\text{O}_3^{\text{T}} + \text{MgO}$  of 4.34–9.70 wt% and  $\text{Mg}^{\#}$  values of 47–56, ALK values of 4.95–6.08 wt%, low  $\text{TiO}_2$  of 0.44–0.62 wt% and relatively high  $\text{Al}_2\text{O}_3$  of 11.44–14.00 wt%. The samples have

relatively high L.O.I. values ranging from 2.46 wt% to 4.77 wt%, probably caused by calcites filled in rock fissures. In the TAS (Figure 6A) and  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$  (Figure 6B) diagrams, the samples fall into the dacite-rhyolite field and show calc-alkaline to high-K calc-alkaline characteristics.

#### 4.2.2 Trace elements

Samples from the Yuechengling and Damingshan plutons have similar trace element compositions, which suggests the similarity of



their petrogenesis. In the primitive mantle-normalized trace element spider diagrams (Figure 6C), all the samples show relatively enrichment of large ion lithophile elements (LILEs, e.g., Rb, Th, U, K) and Pb, relative depletion of Ba, Sr, and high field strength elements (HFSEs, e.g., Nb, Ta, P, Ti), and no Zr and Hf anomalies. These features are similar to those of Early Paleozoic granitoids from Yuechengling (Lin et al., 2017).

The samples have total rare Earth element ( $\Sigma$ REE) values of 124–181 ppm, relatively enrichment in light rare Earth elements (LREEs, Figure 6D), and relatively depletion in heavy rare Earth elements (HREEs, Figure 6D), with the LREE/HREE ratios ranging from 7.53 to 10.43 (Supplementary Table S2). The chondrite-normalized REE patterns (Figure 6D) show that the samples have right-inclined HREE patterns, with  $La_N/Yb_N$  ratios ranging from 8.72 to 12.24, which indicate weak-moderate fractionation between HREEs and LREEs. Besides, the samples exhibit moderate negative Eu anomalies with  $\delta Eu$  values of 0.63–0.75 [Figure 6D, Supplementary Table S2,  $\delta Eu = Eu_N/(Sm \times Gd)^{1/2}$ ], which suggest that there might be plagioclase residue in the source area or its parental magma suffered plagioclase fractionation during its evolution.

### 4.3 Zircon Lu-Hf isotope

As shown in Supplementary Table S3, *In situ* Lu-Hf isotope analyses of zircons that have  $\geq 90\%$  concordance U-Pb ages have been carried out.  $^{176}Lu/^{177}Hf$  ratios of the zircon grains range from 0.000015 to 0.002425. Most of them have  $^{176}Lu/^{177}Hf$  ratios less than

0.002, indicating no accumulation of radiogenic Hf after zircon formation and the ratios of Hf isotopes are not affected by later episodes of partial melting and fractional crystallization, the ratios can essentially represent the Lu-Hf system when the zircon formed (Wu et al., 2007).

#### 4.3.1 The Yuechengling granitoids

Thirteen zircons from sample 21LDT-1 (granodiorite) with concordant ages of 460–432 Ma display uniform ( $^{176}Lu/^{177}Hf$ )<sub>i</sub> (initial ratio) values of 0.282298–0.282422 (Figure 7A), negative  $\epsilon_{Hf}(t)$  values ranging from –7.49 to –3.12, and two-stage Hf isotope model ages ( $T_{DM2}$ ) of 1.88–1.60 Ga (Figure 7B). Two inherited or captured zircons with ages of 549 and 859 Ma yielded ( $^{176}Lu/^{177}Hf$ )<sub>i</sub> values of 0.282414 and 0.281963 (Figure 7A), negative  $\epsilon_{Hf}(t)$  values of –0.90 and –9.89,  $T_{DM2}$  ages of 2.37 and 1.55 Ga (Figure 7B), respectively.

The Lu-Hf analyses were performed on 14 Early Paleozoic (475–431 Ma) zircons from sample 21LDT-2-01 (granodiorite), and these zircons show ( $^{176}Lu/^{177}Hf$ )<sub>i</sub> values of 0.282278–0.282388 (Figure 7A), corresponding to negative  $\epsilon_{Hf}(t)$  values of –8.24 to –4.33 and  $T_{DM2}$  age of 1.92–1.68 Ga (Figure 7B). The oldest zircon (754 Ma) display relatively high ( $^{176}Lu/^{177}Hf$ )<sub>i</sub> value of 0.282188 (Figure 7A), negative  $\epsilon_{Hf}(t)$  value of –4.28, and  $T_{DM2}$  age of 1.93 Ga (Figure 7B).

Fifteen zircons from sample 21LDT-2-02 (granodiorite) with the ages of 481–439 Ma were analyzed, results show that they have similar characteristics to the granitoid samples above, which contains ( $^{176}Lu/^{177}Hf$ )<sub>i</sub> values of 0.282171–0.282379 (Figure 7A)

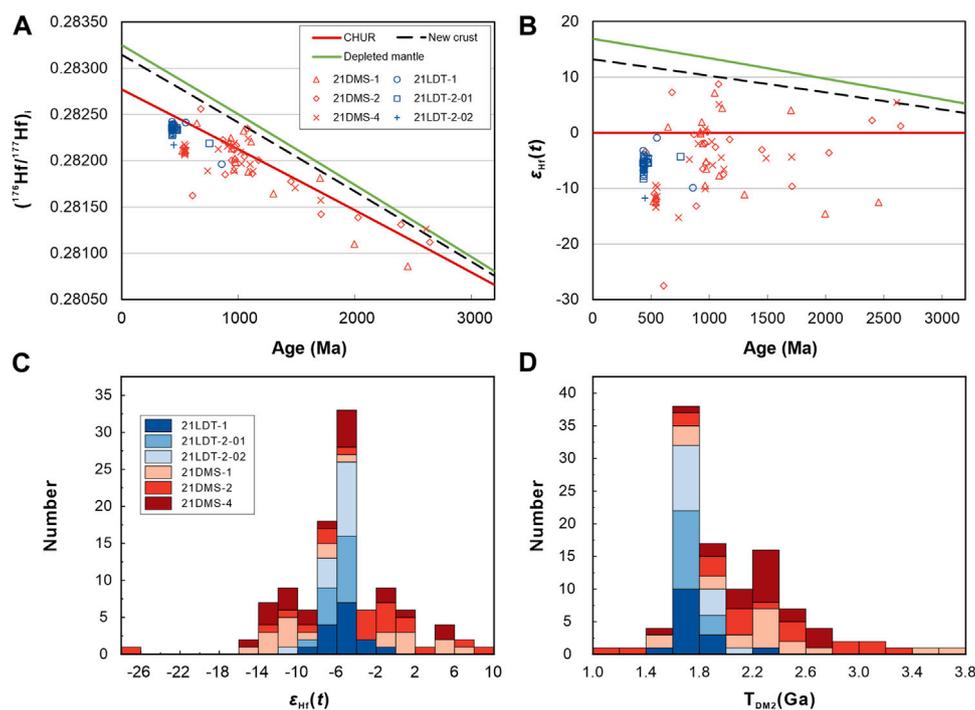


FIGURE 7

Diagrams of Lu-Hf isotopic data for zircons from the Yuechengling granitoids and the Damingshan volcanoclastic rocks. Plots of (A) U-Pb ages vs.  $(^{176}\text{Lu}/^{177}\text{Hf})_i$ , (B) U-Pb ages vs.  $\epsilon_{\text{Hf}}(t)$ , Histograms of (C)  $\epsilon_{\text{Hf}}(t)$  values and (D) Hf isotope two-stage model ages.

that correspond to negative  $\epsilon_{\text{Hf}}(t)$  values ranging from  $-11.98$  to  $-4.43$  and  $T_{\text{DM2}}$  ages of  $2.16$  to  $1.70$  Ga (Figure 7B).

### 4.3.2 The Damingshan volcanoclastic rocks

Five zircons with the ages of  $542$ – $521$  Ma from sample 21DMS-1 (volcanic breccia) show consistent  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values ranging from  $0.282090$  to  $0.282125$  (Figure 7A), with negative  $\epsilon_{\text{Hf}}(t)$  values of  $-12.53$  to  $-11.27$ , and  $T_{\text{DM2}}$  ages of  $2.28$  to  $2.20$  Ga (Figure 7B), while 13 Mesoproterozoic-Neoproterozoic ( $1703$ – $645$  Ma) zircons have  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values ranging from  $0.281646$  to  $0.282406$  (Figure 7A), with both negative and obviously positive  $\epsilon_{\text{Hf}}(t)$  values ranging from  $-11.10$  to  $7.18$ , corresponding to variable  $T_{\text{DM2}}$  ages ranging from  $2.79$  to  $1.43$  Ga (Figure 7B). The remaining Early Paleoproterozoic ( $2,455$  Ma) and Late Paleoproterozoic ( $1996$  Ma) zircons have  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values of  $0.280859$  and  $0.281099$  (Figure 7A), obviously negative  $\epsilon_{\text{Hf}}(t)$  values of  $-12.48$  and  $-14.58$ ,  $T_{\text{DM2}}$  ages of  $3.79$  and  $3.56$  Ga (Figure 7B), respectively.

The youngest ( $451$  Ma) and the other Early Paleozoic ( $528$  Ma) zircons from sample 21DMS-2 (volcanic breccia) display  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values of  $0.282404$ – $0.282142$  (Figure 7A), corresponding to negative  $\epsilon_{\text{Hf}}(t)$  values of  $-3.42$  to  $-10.99$  and  $T_{\text{DM2}}$  ages of  $2.17$ – $1.63$  Ga (Figure 7B). 15 zircons with Mesoproterozoic-Neoproterozoic ages ( $1712$ – $608$  Ma) yielded higher  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values vary from  $0.281422$  to  $0.282561$  (Figure 7A), extremely negative to obviously positive  $\epsilon_{\text{Hf}}(t)$  values of  $-27.54$  to  $8.73$ , and variable  $T_{\text{DM2}}$  ages vary from  $3.26$ – $1.13$  Ga (Figure 7B). The remaining three Neoproterozoic-Paleoproterozoic zircons with ages from  $2,644$  Ma to  $2028$  Ma show a narrow range of  $(^{176}\text{Lu}/^{177}\text{Hf})_i$

values ( $0.281118$ – $0.281386$ ) (Figure 7A), corresponding to both negative and positive  $\epsilon_{\text{Hf}}(t)$  values of  $-3.63$  to  $2.22$ , and  $T_{\text{DM2}}$  ages of  $3.08$ – $2.82$  Ga (Figure 7B).

In sample 21DMS-4 (volcanic breccia), 7 zircons with the ages of  $552$  Ma to  $540$  Ma have  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values of  $0.282065$ – $0.282177$  (Figure 7A), obviously negative  $\epsilon_{\text{Hf}}(t)$  values of  $-13.38$  to  $-9.43$ , and  $T_{\text{DM2}}$  ages of  $2.33$ – $2.08$  (Figure 7B), respectively. 12 Mesoproterozoic-Neoproterozoic ( $1708$ – $737$  Ma) zircons exhibit variable  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  values ( $0.281573$ – $0.282242$ ) (Figure 7A) that correspond to obviously negative to positive  $\epsilon_{\text{Hf}}(t)$  values of  $-15.26$  to  $5.08$  and variable  $T_{\text{DM2}}$  ages ( $2.69$ – $1.59$  Ga) (Figure 7B). The oldest zircon with a Neoproterozoic age of  $2,610$  Ma shows the lowest  $(^{176}\text{Lu}/^{177}\text{Hf})_i$  value of  $0.281260$ , corresponding to the highest positive  $\epsilon_{\text{Hf}}(t)$  value of  $5.45$  and the oldest  $T_{\text{DM2}}$  age of  $2.78$  Ga (Figure 7B).

## 5 Discussion

### 5.1 Formation age of the igneous rocks

Salient information from previous geochronological studies of the Early Paleozoic igneous rocks from the SCB have been reported in the past few years, showing that the igneous rocks were formed between ca.  $460$  Ma and ca.  $390$  Ma, and peaked at ca.  $440$ – $420$  Ma (Li et al., 2011; Wang et al., 2013b; Xin et al., 2020; Kong et al., 2021; Tang et al., 2021 and the related references). Previous studies based on the Early Paleozoic granitoids from the Yuechengling pluton were aged by using LA-ICP-MS zircon U-Pb (Zhao et al., 2013; Chen

et al., 2016; Lin et al., 2017; Chen et al., 2018), zircon SHRIMP U-Pb (Bai et al., 2015), and SIMS zircon U-Pb (Chu et al., 2012) dating methods and obtained age data displaying a wide emplacement age peaked at 435–422 Ma. Our new LA-ICP-MS zircon U-Pb age data further constrain the emplacement age of the granitoids from the Yuechengling pluton to be 438–436 Ma.

In contrast, very few geochronological studies have been conducted for the Early Paleozoic igneous rocks from the Damingshan area, with the reported ages of 441–432 Ma for the granitoids (Chen, 2018; Wang et al., 2020), but a vacancy for the volcanoclastic rocks. In this study, zircons from the volcanoclastic rocks are mainly inherited or captured zircons, and the youngest concordant zircons from three samples are  $521 \pm 6$ ,  $451 \pm 4$ , and  $540 \pm 6$  Ma, respectively. Since the volcanoclastic rocks are commonly deposited soon after a volcanic eruption, its deposited age would be close to the volcanic eruption age. And the volcanic eruption age could be constrained by the youngest group or single igneous zircon age in the volcanoclastic rocks. Consequently, we suggest that the volcanoclastic rocks should be formed by an Early Paleozoic volcanic eruption which is later than 451 Ma. In addition, the inherited zircons from Neoproterozoic to Neoproterozoic indicated that ancient materials might exist in their source region.

In summary, the emplacement age of the Yuechengling granitoids constrained to be ca. 437 Ma while the deposited age of the Damingshan volcanoclastic rocks to be later than 451 Ma.

## 5.2 Genetic type of the Yuechengling granitoids

The granites are commonly divided into I-, S-, and A-types according to the nature of protolith and petrographical and geochemical features (Chappell and White, 1974; Loiselle and Wones, 1979). Studies have shown that feldspar is mostly alkali feldspar in A-type granites, often albite-orthoclase solid solutions or intergrowths, and micrographic intergrowths of quartz and alkali feldspars are very common (Collins et al., 1982). However, the Yuechengling granitoids consist of quartz, plagioclase, K-feldspar, biotite, magnetite, and apatite, being inconsistent with the typical petrographic characteristics of A-type granites. Compared with I-type and S-type granites, A-type granites can be distinguished from their high Zr + Nb + Ce + Y contents (average value = 350 ppm) and  $\text{FeO}^{\text{T}}/\text{MgO}$  ratios (average value = 10), and enrichment in HFSEs (e.g., Nb and Ta) (Whalen et al., 1987). Geochemical data of the Yuechengling granitoids display low Zr + Nb + Ce + Y contents (246–275 ppm; average value = 257) and low  $\text{FeO}^{\text{T}}/\text{MgO}$  ratios (1.84–1.93; average value = 1.87) (Supplementary Table S2), lower than the limit and being inconsistent with the Fe-rich characteristics of A-type granites (Whalen et al., 1987). The depletion of HFSEs (Nb, Ta, P, Ti) is also different from typical A-type granites but similar to I- and S-type granites (Figure 6C). Moreover, all the granitoids from this study fall in the range of unfractionated and fractionated I- and S-type granites on the Zr + Nb + Ce + Y vs.  $\text{FeO}^{\text{T}}/\text{MgO}$  (Figure 8A) and Zr + Nb + Ce + Y vs.  $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{CaO}$  diagrams (Figure 8B), which resembles the Yuechengling granitoids reported by Chen et al. (2016), Cheng et al. (2016), and Chen et al. (2018), with only a few samples showing A-type

characteristics which could be produced by strong fractionated S- or I- type granites (Champion and Bultitude, 2013).

I-type and S-type granites have similar mineralogical and geochemical compositions, yet there are some differences. I-type granites contain hornblende and pyroxene, with normative mineral C (Corundum) content of  $< 1$  (Chappell and White, 1974). The granitoids from this study do not have a mineralogy typical of I-type granites, all the studied samples do not contain hornblende or pyroxene with normative mineral C contents of  $> 1$  (2.80–5.87; average value = 3.89). Furthermore, I-type granites are metaluminous to weakly peraluminous (A/CNK value  $< 1.1$ ) and have relatively high  $\text{Na}_2\text{O}$  contents ( $> 3.2$  wt%; Chappell and White, 1992). The studied granitoids are all strongly peraluminous granitoids, with high A/CNK values of 1.18–1.55 (average value = 1.32, with all  $> 1.1$ ), A/NK values of  $> 1.0$  (1.77–2.00; average value = 1.85), and relatively low  $\text{Na}_2\text{O}$  contents ranging from 2.78 to 3.13 wt% (average value = 2.90 wt%, all  $< 3.2$  wt%; Supplementary Table S2), which are typical characteristics of S-type granites. Moreover, on the  $\text{SiO}_2$  vs.  $\text{FeO}^{\text{T}}/(\text{FeO}^{\text{T}} + \text{MgO})$  (Figure 8C) and ACF diagrams (Figure 8D), the granitoids are all distributed in the S-type range, which is similar to previous studies from the Yuechengling pluton, furthering S-type affinity.

## 5.3 Origin of the Early Paleozoic igneous rocks

### 5.3.1 The Yuechengling granitoids

S-type granites are usually characterized by felsic compositions with low Fe + Mg contents less than 3%–4% at reasonable crustal pressures and temperatures (Champion and Bultitude, 2013 and references therein), while the Yuechengling granitoids display high-maficity feature with relatively high Fe + Mg contents of 5.98–6.31 wt%. Several different mechanisms of this feature have been proposed, including 1) source heterogeneity, especially heterogeneous continental crustal material sources (e.g., Villaros et al., 2012); 2) magma mixing, incorporation of mantle-derived mafic magma will lead to mafic feature (Clemens et al., 2011; Champion and Bultitude, 2013); 3) selective entrainment of peritectic/restitic and accessory minerals, especially the peritectic garnet (e.g., Zhu et al., 2020; Song and Xu, 2022); 4) hydrothermal alteration, the hydrothermal fluids can bring Fe and Mg components into the granites (e.g., Song and Xu, 2022). Since no peritectic/restitic garnet was contained in the Yuechengling granitoids (Table 1), the mechanism of the entrainment of peritectic garnet was excluded. Thus, a full assessment of the partial melting, source heterogeneity, magma mixing, and fractional crystallization in the magmatic evolution process and the post-magmatic hydrothermal alteration could be accounted for petrogenesis and high-maficity feature of the Yuechengling granitoids.

#### 5.3.1.1 Partial melting and source heterogeneity

Zircon Lu-Hf isotope is of great significance for the study of magmatic evolution and source tracing, since it has extremely high closure temperature, which can maintain primitive Hf isotopic composition even under high-grade metamorphic conditions (Wu et al., 2007). The Yuechengling granitoids have negative  $\epsilon_{\text{Hf}}(t)$  values ranging from  $-11.98$  to  $-0.90$ , and corresponding

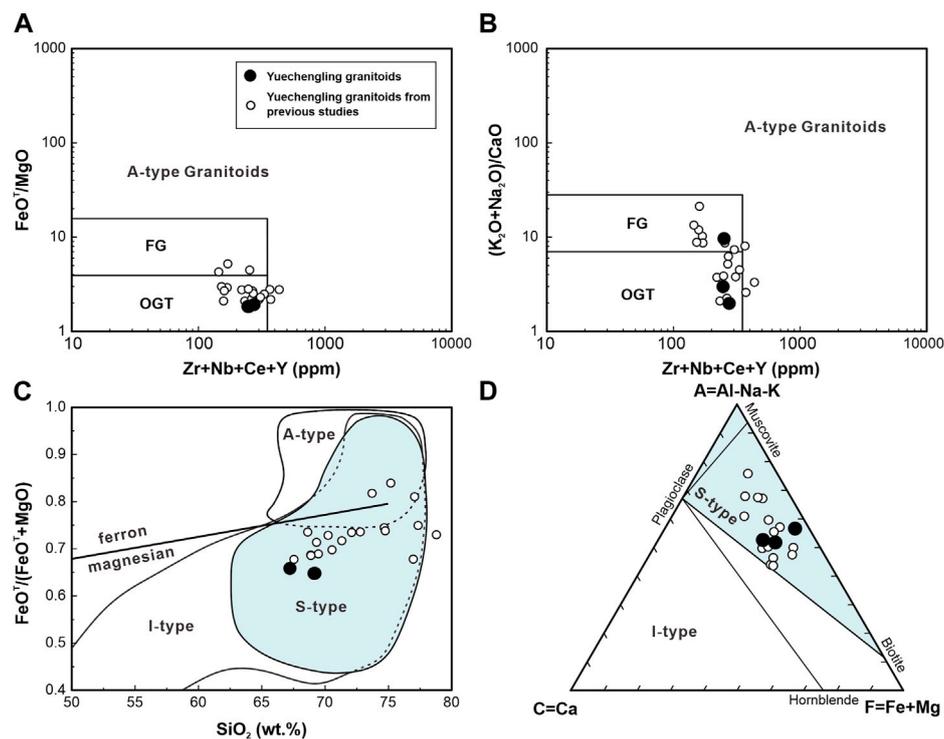


FIGURE 8

Petrogenetic discrimination diagrams of the Yuechengling granitoids: (A) Zr + Nb + Ce + Y vs.  $\text{FeO}^{\text{T}}/\text{MgO}$ ; (B) Zr + Nb + Ce + Y vs.  $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{CaO}$ , (C)  $\text{SiO}_2$  vs.  $\text{FeO}^{\text{T}}/(\text{FeO}^{\text{T}} + \text{MgO})$ , (D) ACF diagram. FG-fractionated M-, I-, and S-type granites; OGT-unfractionated M-, I-, and S-type granites. (A,B) are after Whalen et al. (1987), (C) is after Frost et al. (2001), (D) is after Chappell and White (1992). Previous data of Yuechengling granitoids are from Chen et al. (2016), Cheng et al. (2016), and Chen et al. (2018).

$T_{\text{DM2}}$  ages distributed from 2.37 to 1.55 Ga (Figures 7B–D; Supplementary Table S3), indicating that they might be derived from a crustal source of Paleoproterozoic basement. The granitoids have Rb/Sr ratios ranging from 0.95 to 1.25 (average value = 1.1), which are higher than the mantle-derived granitoids (Rb/Sr < 0.05) and crust-mantle-sourced granitoids (Rb/Sr = 0.05–0.50), but consistent with the range of crust-derived granites (Rb/Sr > 0.5; Sylvester, 1998). They have Nb/Ta ratios (7.89–8.4, average = 8.21) that close to the average value of continental crust (Nb/Ta = 11) and significantly less than the average value of primitive mantle (Nb/Ta = 17.8; Sylvester, 1998). All the granitoids are characterized by depletion of Nb, Ti and enrichment of Pb (Figure 6C), which furthered a crustal source.

There is little controversy about the sources of peraluminous, crustal-evolved, S-type granitic magma, which are derived from partial melting of meta-sedimentary rocks (Clemens et al., 2011). However, some scholars have shown that some S-type granitoids in the SCB are derived from a heterogeneous source (e.g., Zhu et al., 2020). The studied granitoids contained high  $\text{Al}_2\text{O}_3$  contents (14.97–16.30 wt%) and show peraluminous characteristics ( $A/\text{CNK}$  value = 1.18–1.55, Supplementary Table S2), which can be produced by fractional crystallization of hornblende from subaluminous melts ( $A/\text{CNK}$  value < 1, Zen, 1986) or partial melting of meta-igneous source rocks (Reichardt and Weinberg, 2012). However, combining with previous studies, the  $A/\text{CNK}$  values of the Yuechengling granitoids are constant with the

increase of  $\text{SiO}_2$  contents (Figure 9A) and show negative Eu anomalies (Figure 6D), being inconsistent with fractional crystallization of hornblende from subaluminous melts (Jiang and Zhu, 2017). Moreover, melts produced by partial melting of meta-igneous source rocks usually display enrichments in Na ( $\text{K}_2\text{O}/\text{Na}_2\text{O} < 1$ ), Sr ( $\text{Sr}/\text{Rb} > 10$ ), and Eu ( $\delta\text{Eu} > 1$ ) (Reichardt and Weinberg, 2012). Our samples contain high  $\text{K}_2\text{O}/\text{Na}_2\text{O}$  ratios (1.11–1.26), low Sr/Rb ratios (0.8–1.06) and display depletion in Eu (Supplementary Table S2; Figure 6C), excluding partial melting of meta-igneous source rocks. Generally, melts derived from metapelite show relatively low  $\text{CaO}/\text{Na}_2\text{O}$  ratios of < 0.3 and metagreywacke-derived melts contain higher  $\text{CaO}/\text{Na}_2\text{O}$  ratios of 0.3–1.5 (Sylvester, 1998), and granitoids of this study have variable  $\text{CaO}/\text{Na}_2\text{O}$  ratios of 0.22–1.11. Combining with previous data, on the Rb/Sr vs.  $\text{CaO}/\text{Na}_2\text{O}$  and Rb/Sr vs. Rb/Ba diagrams (Figures 9C, D), the Yuechengling granitoids are distributed both in the ranges of clay-poor and clay-rich sources, demonstrating the granitoids might be the products of pelite and greywacke melting. In summary, we suggest heterogeneity of meta-sedimentary sources may contribute to the granitoids, and they are derived from a crustal source with both meta-greywacke and meta-pelite components of the ancient basement.

### 5.3.1.2 Magma mixing and hydrothermal alteration

Recently, a growing number of the Early Paleozoic ultramafic rocks have been reported in the SCB (e.g., Wang et al., 2013b;

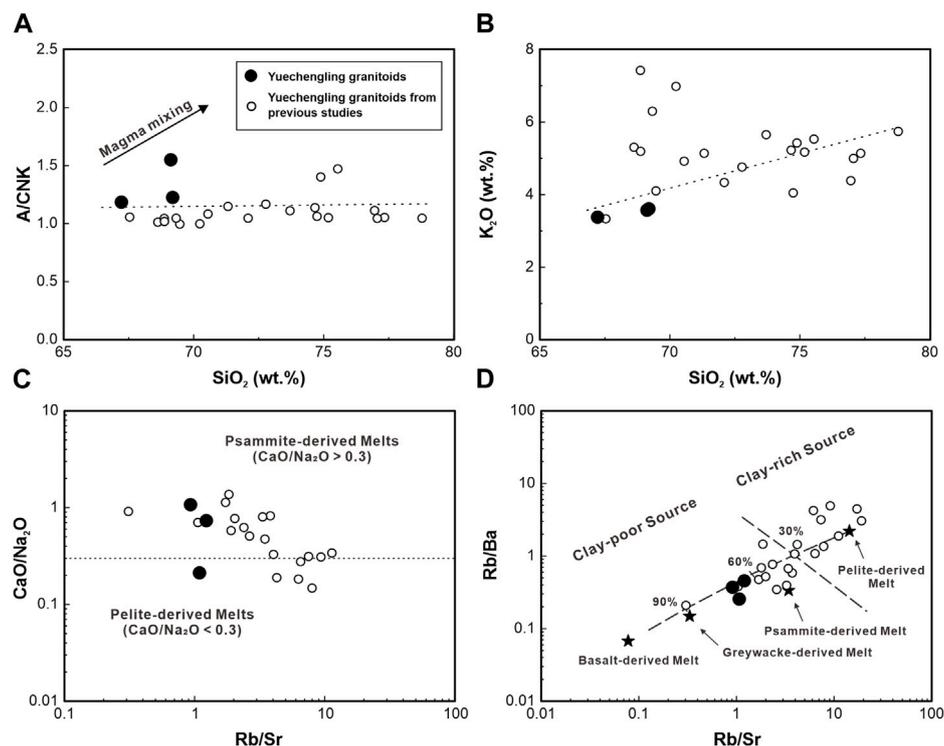


FIGURE 9

Petrogenetic discrimination diagrams of the Yuechengling granitoids. (A)  $\text{SiO}_2$  vs.  $A/CNK$ , (B)  $\text{SiO}_2$  vs.  $\text{K}_2\text{O}$ , (C)  $\text{Rb}/\text{Sr}$  vs.  $\text{CaO}/\text{Na}_2\text{O}$ , (D)  $\text{Rb}/\text{Ba}$  vs.  $\text{Rb}/\text{Sr}$ . (C) is after Li et al. (2003), (D) is after Sylvester (1998). Previous data of Yuechengling granitoids are from Chen et al. (2016), Cheng et al. (2016), and Chen et al. (2018).

Zhong et al., 2013; 2014; 2016; Zhang et al., 2015), indicating mantle-derived materials involved in generation of the subaluminous felsic magma, and the incorporation of mantle-derived mafic magma will trigger more mafic features such as high ferromagnesian contents of the melts (Clemens et al., 2011). Magma mixing process has been widely discussed on the genesis of the Early Paleozoic granitoids in the SCB, with inputting of mantle-derived materials (e.g., Zhang et al., 2012; Xia et al., 2014; Tang et al., 2021). Generally, variable zircon  $\varepsilon_{\text{Hf}}(t)$  values ranging from negative to positive are considered as a result of mixing between crust- and mantle-derived magma (e.g., Xia et al., 2014). However, the Yuechengling granitoids have negative  $\varepsilon_{\text{Hf}}(t)$  values ( $-11.98$  to  $-0.90$ ), which indicates that they were derived from a crustal source with no significant mixing between crust- and mantle-derived magma. Granitoids with high  $\text{Mg}^\#$  values (commonly  $> 50$ ) are possibly having a contribution of mantle-derived components to their parental magma (e.g., Abdallsamed et al., 2017). Samples of this study have  $\text{Mg}^\#$  values of 48–49 (all  $< 50$ ), furthering no mixing occurred. Moreover, on the  $\text{SiO}_2$  vs.  $A/CNK$  (Figure 9A) diagram, they do not display an obvious trend of magma mixing combining our new data with previous studies. These evidences indicate no certain degree of magma mixing, suggesting that mantle-derived materials were not involved and the model of magma mixing is excluded.

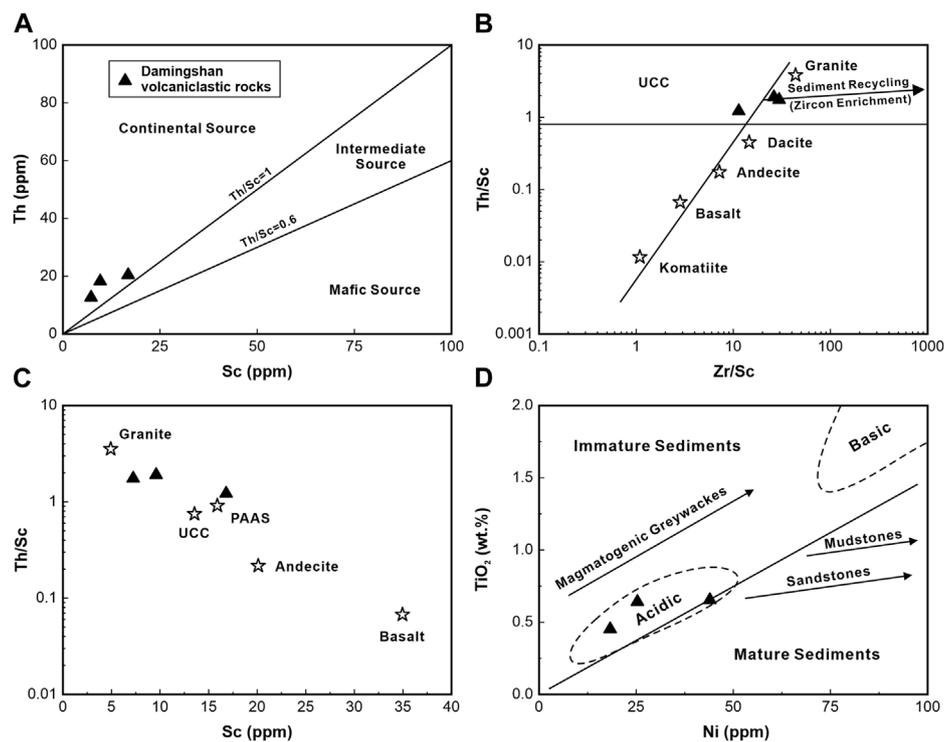
Studies have shown that post-magmatic tectonic-thermal events can lead S-type granites to more mafic features, the hydrothermal

fluids can bring Fe and Mg components into granites (e.g., Song and Xu, 2022). The granitoids from our study exhibit kaolinization and chloritization of K-feldspar and biotite, respectively, accompanied by sericitization of plagioclase. These petrographic characteristics indicate that they have been modified by variable degrees of intermediate- and low-temperature hydrothermal alteration. At the same time, hornblende can retrogress to biotite under hydrothermal conditions, which explains the absence of hornblende in the granodiorite samples. Moreover, most of the deposits in the Yuechengling area are considered related to magmatic-hydrothermal activities (Wu et al., 2012; Chen et al., 2016). Thus, the hydrothermal alteration can be the most reasonable explanation for the high-maficity feature of the granitoids in this paper. It should be noted that the proportion of Mg component in the hydrothermal fluids might be relatively high, by the reason of our samples contain relatively high  $\text{Mg}^\#$  values nearly close to 50 and no mantle-derived materials were involved in their magma source.

However, due to the existence of coetaneous mantle-derived magmatic products in the SCB, the high-maficity feature of the Yuechengling S-type granitoids is attributed to the involvement of mantle-derived materials or the alteration of hydrothermal fluids should be further examined in future studies.

### 5.3.1.3 Fractional crystallization

On the  $\text{Zr} + \text{Nb} + \text{Ce} + \text{Y}$  vs.  $\text{FeO}^\text{T}/\text{MgO}$  (Figure 8A) and  $\text{Zr} + \text{Nb} + \text{Ce} + \text{Y}$  vs.  $(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{CaO}$  diagrams (Figure 8B), the samples all



**FIGURE 10**

Diagrams of (A) Sc vs. Th, (B) Zr/Sc vs. Th/Sc, (C) Sc vs. Th/Sc, and (D) Ni vs.  $\text{TiO}_2$ . (A) is after Nagarajan et al. (2015), (B) is after McLennan et al. (1993), averages of the rocks are after Roser et al. (2002), (C) is after Nagarajan et al. (2015), (D) is after Floyd et al. (1990). PASS-Post-Archean Australian Shales; UCC-Upper Continental Crust.

fall into the weakly fractionated granitoid field, indicating some degree of fractional crystallization. The granitoids have low contents of  $\text{SiO}_2$  (66.12–67.32 wt%) and Differentiation index (DI) (73.46–84.96) and ratios of Rb/Sr (0.95–1.25), high ratios of K/Rb (135–184) (Supplementary Table S2), demonstrating a limited fractional crystallization (Sami et al., 2020).

Fractional crystallization or residual of plagioclase can be indicated by depletion of Eu (Figure 6D). Nb and Ti are commonly hosted in Ti-bearing minerals (e.g., ilmenite and titanite), the depletion of Nb and Ti are indicative of the fractional crystallization of Ti-bearing minerals and a crustal magma source (Figure 6C). The depletion of P (Figure 6C) and low contents of  $\text{P}_2\text{O}_5$  (0.11–0.13 wt%, Supplementary Table S2) are related to fractionation of apatite (Healy et al., 2004). Moreover, the increases in  $\text{K}_2\text{O}$  contents with increasing  $\text{SiO}_2$  contents show that there was no obvious fractional crystallization of K-feldspar and biotite (Figure 9B). Therefore, the Yuechengling granitoids have undergone some degree of fractional crystallization of plagioclase, Ti-bearing minerals, and apatite.

## 5.3.2 The Damingshan volcaniclastic rocks

### 5.3.2.1 Weathering and sediment recycling.

The chemical index of alteration (CIA) [ $\text{CIA} = \text{molar Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100$ ] is often used as an important parameter to reveal weathering degree of source rocks (Nesbitt and Young, 1982). Generally, rocks with CIA values of 45–55 show low

degree of weathering (CIA of the crust is ca. 47) and value of 100 to be intense degree of weathering, with the alkali and alkaline Earth elements no longer retained (McLennan et al., 1993). The Damingshan volcaniclastic rocks have CIA values ranging from 52 to 61 with an average value of 57 (Supplementary Table S2), indicating incipient weathering conditions. These rocks have maturity index  $\text{Al}_2\text{O}_3 / (\text{Na}_2\text{O} + \text{K}_2\text{O})$  values of limited variation of 2.30–2.44, showing similar and low maturity and proximal sources.

Th and Zr are incompatible elements in the symbiotic components of igneous rocks and are often enriched in felsic rocks, whereas Sc often contained as a compatible element in the mafic mineral components in the initial stage of magmatic evolution (McLennan and Taylor, 1991). The ratio of Th/Sc is considered to be an indicator of revealing average provenance and enrichment degree of zircon (heavy-mineral), which will increase with the sediment recycling process (McLennan et al., 1993). In the Zr/Sc vs. Th/Sc diagram (Figure 10B), the volcaniclastic rocks are distributed along the compositional variation trend, indicating a low degree of sediment recycling and heavy-mineral sorting. Thus, the geochemistry data of the volcaniclastic rocks are valid for further discussion.

### 5.3.2.2 Provenance

For clastic sedimentary rocks that have not undergone significant sediment recycling, their geochemistry

characteristics can be used for distinguishing between mafic/ultramafic and felsic source materials (Taylor and McLennan, 1985; Wronkiewicz and Condie, 1987).  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios could be used to discriminate the characteristics of source rocks, with mafic rocks having low  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios of 3–8, intermediate rocks of 8–21 and felsic rocks of higher ratios (21–70) (Hayashi et al., 1997). Volcaniclastic rocks of this study have relatively high  $\text{Al}_2\text{O}_3/\text{TiO}_2$  ratios of 19.4–26.1, suggesting intermediate to felsic components in the source area. On the Th vs. Sc plot, the rocks concentrate in the field of continental sources (Figure 10A). On the Th/Sc vs. Zr/Sc diagram (Figure 10B), the samples distributed between the dacite and granite fields. On the Sc vs. Th/Sc diagram (Figure 10C), they concentrate between andesite and granite which are closer to granite field. Combining with Ni vs.  $\text{TiO}_2$  diagram (Figure 10D), the rocks were suggested to be acidic rather than mafic. The REE contents and Eu anomalies of clastic sedimentary rocks are also important keys for source rock characteristics (Xiang et al., 2015). Mafic rocks have lower LREE/HREE ratios and no negative Eu anomalies, whereas felsic rocks generally have higher LREE/HREE ratios and negative Eu anomalies (Yan et al., 2012). The samples have relatively high LREE/HREE ratios ranging from 7.53 to 9.12 with average value of 8.27 (Supplementary Table S2), and exhibit moderate negative Eu anomalies (Figure 6D), also indicating mainly felsic sources. The plots are consistent with the interpretation that the principal source rocks were of felsic composition with some intermediate composition included. The inference is also supported by mineral assemblages (Table 1; Figure 3).

Zircon grains from our samples exhibit mostly negative  $\epsilon_{\text{Hf}}(t)$  values with partially positive (−27.54 to 8.73, Figures 7B, C), indicating that they were dominantly derived from crustal material and may have undergone some degree of magma mixing with mantle-derived materials. Moreover, the relatively high  $\text{Mg}^\#$  values (47–56, Supplementary Table S2) of the samples also indicate the contribution of mantle-derived components. Zircons with negative  $\epsilon_{\text{Hf}}(t)$  values (−27.54 to −0.14) show  $T_{\text{DM2}}$  ages of 3.79 to 1.63 Ga, suggesting that they were mainly derived from Archean-Mesoproterozoic crustal materials. Therefore, combined with petrographic and geochemical data, we suggest that the felsic parental magma was erupted to the surface in a Late Ordovician volcanic event (later than 451 Ma) and deposited soon after the eruption.

## 5.4 Constraints on the Early Paleozoic tectonic evolution of the SCB

Controversy surrounds the tectonic evolution of the Early Paleozoic orogeny in the SCB and two disparate tectonic models have been presented: 1) intracontinental orogeny (Charvet et al., 2010; Xia et al., 2014; Shu et al., 2015; Faure et al., 2017; Tang et al., 2021), i.e., the Yangtze and Cathaysia Blocks were amalgamated together into the ancient South China continent during the amalgamation process of the Rodinia supercontinent in the Late Neoproterozoic, and the Early Paleozoic “Huanan Ocean” did not exist. 2) oceanic subduction-collision (Qin et al., 2011; Peng et al., 2016a;

Peng et al., 2016b; Liu et al., 2018), i.e., the “Huanan Ocean” existed and oceanic subduction occurred in the SCB in the Early Paleozoic.

As absence of the Early Paleozoic ophiolites, island arc igneous rock, coeval HP/LT (high pressure-low temperature)-type metamorphic rocks and turbidite with “Bouma sequence” related to closure of the “Huanan Ocean” are lacking in the SCB, the intra-continental orogenic model has been widely accepted (e.g., Charvet et al., 2010; Wang et al., 2011; Shu et al., 2014). Meanwhile, some “Early Paleozoic island arc igneous rock” and “ophiolite suites” from the southwest segment of the Jiangnan Orogen have been reported recently. Based on geochemical, petrological and geochronological studies, the existence of the Early Paleozoic “Huanan Ocean” and several different subductional-collisional models have been proposed (Peng et al., 2016a; Peng et al., 2016b; Qin et al., 2017). However, the origin of igneous rock with subductional signature is uncertain. The Early Paleozoic igneous rocks in the SCB generally show depletion of HFSEs (e.g., Nb and Ta), which is geochemically similar to island arc magma, and were considered to be formed in a subductional-collisional setting (Qin et al., 2011; Qin et al., 2017). However, the interpretation of “subductional signature” is not only applied to island arc magma. In some cases, the depletion of Nb and Ta can be caused by some magmatism related to intra-plate rift (Rudnick and Gao, 2003; Murphy and Dostal, 2007), or magma derived from the melting of ancient island arc material (Li et al., 2005), lithosphere mantle, or contamination of crustal materials (Zhang X. S. et al., 2017). Furthermore, the complete sequence and age of the Early Paleozoic “ophiolite suit” are uncertain. Although a suit of the Early Paleozoic “ophiolite” was found in the Nuodong area of the SCB (Peng et al., 2016a), it lacks the ultramafic rock (mantle peridotite) unit and should be excluded from the standard ophiolite suit. In addition, some “Early Paleozoic ophiolite” in the SCB was confirmed to be formed in Neoproterozoic (Li et al., 2005; Shu et al., 2006). Thus, further work is needed to refine the integrity and age of the “ophiolite suit”.

Igneous rocks formed in the subductional-collisional setting generally display a linear distribution (Zhang et al., 2013). Compared with the Late Mesozoic granites in the SCB (Li and Li, 2007), the spatial and temporal distribution of the Early Paleozoic granites does not display a clear trend of gradually younger age from inland to coastal caused by the plate retracement (Liu X. et al., 2020). From southeast to northwest, the SCB displays uninterrupted detrital zircon ages and sedimentary facies of the Lower Paleozoic sedimentary rocks (Wang et al., 2010; Yu et al., 2015). Combining with biostratigraphy, paleocurrent, and paleoecology signature (Chen et al., 2010; Shu et al., 2014; Yu et al., 2015), it is suggested that the Yangtze and Cathaysia Blocks were not separated in the Early Paleozoic.

Moreover, there is no sufficient geochemical evidence for the existence of asthenosphere mantle-derived igneous rock. The Early Paleozoic mafic igneous rocks reported in the SCB are characterized by extremely low  $\epsilon_{\text{Hf}}(t)$  and  $\epsilon_{\text{Nd}}(t)$  values and show depletions in HFSEs (e.g., Nb and Ta), which is similar to igneous rocks of the lithospheric mantle source (Jia et al., 2017). Therefore, the Yuechengling granitoids and Damingshan volcaniclastic rocks were probably formed in an intra-continental setting rather than a subductional-collisional setting.

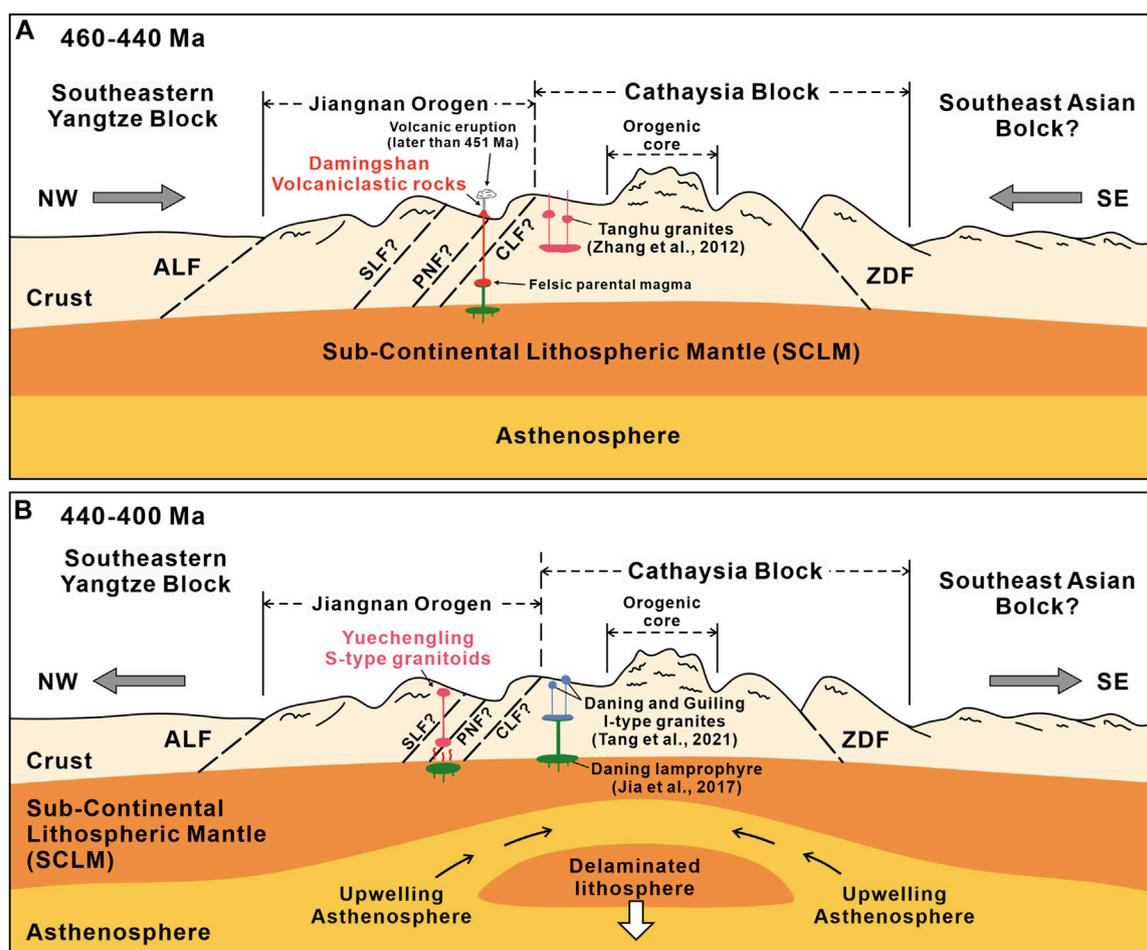


FIGURE 11

Cartoon showing the petrogenetic mechanisms that led to the formation of the Early Paleozoic igneous rocks in the SCB during (A) 460 to 440 Ma and (B) 440 to 400 Ma (modified after Tang et al., 2021 and Yao et al., 2012). ALF—the Anhua-Luocheng fault, CLF—the Chenzhou-Linwu fault (after Zhao, 2015), PNF—the Pingxiang-Gongcheng-Nanning fault (after Zhou and Wen, 2021), SLF—the Shizong-Mile-Luodian fault (after Dong et al., 2015), ZDF—the Zhenghe-Dapu fault.

According to the currently chronological data from the SCB, the Early Paleozoic orogeny in the SCB started in the Late Ordovician (ca. 460 Ma), peaked at the Early-Mid Silurian (ca. 440–420 Ma), and ended in the Early Devonian (ca. 390 Ma) (Li et al., 2011; Wang et al., 2013b; Xin et al., 2020; Kong et al., 2021; Tang et al., 2021 and the related references). It has been accepted that the Early Paleozoic orogeny has undergone two episodes of tectonic stages, including the syn-collisional stage (ca. 460–440 Ma) and post-collisional stage (ca. 440–400 Ma) (Xia et al., 2014; Yu et al., 2016; Cai et al., 2017; Tang et al., 2021).

Generally, the tectonic setting of granites and intermediate rocks has uncertainty, they can be formed in a compressional setting as well as an extensional setting (except for A-type granites). However, peraluminous S-type granites are generally found in settings associated with the syn-collisional or post-collisional stage (Kalsbeek et al., 2001; Atherton and Ghani, 2002). Generally, thickening of the crust, detachment of the subducted slab (Atherton and Ghani, 2002) and lithospheric delamination (Sylvester, 1998) are some of the mechanisms envisaged for the

heat source that led to partial melting of sedimentary rocks to generate S-type granites. In contrast, ultramafic-mafic rocks are normally considered as products of a regional extensional setting, which are important manifestation of deep thermal-dynamic action on the surface. Recently, some mafic-intermediate rocks in the SCB have been reported, such as the Northern Guangdong high-magnesian andesites and dacites (ca. 435 Ma) (Yao et al., 2012), Longhugang ( $423 \pm 8$  Ma), Xinchuan ( $434 \pm 6$  Ma) and Xinsi ( $420 \pm 3$  Ma) gabbroic plutons (Wang et al., 2013b), Dakang gabbroic pluton ( $441.1 \pm 4.7$  Ma) (Zhang et al., 2015), Taoyuan hornblende gabbro ( $409 \pm 2$  Ma) (Zhong et al., 2013), and Daning lamprophyre ( $445 \pm 4$  Ma) (Jia et al., 2017). A-type granites related to extensional setting are also found in the SCB, such as the South Fufang and Yingshang granitoids (ca. 414–404 Ma) (Xin et al., 2020), Xiqin granites (410 Ma) (Cai et al., 2017), Huitong and Epo granites (414–415 Ma) (Feng et al., 2014). Thus, the tectonic setting of the Early Paleozoic orogeny was changed to a strongly extensional environment at least since ca. 445 Ma, and the timing of tectonic transition

might be further constrained to 445–440 Ma based on these Early Paleozoic ultramafic-mafic rocks and A-type granites in the SCB. It is suggested that the Damingshan volcanoclastic rocks (later than 451 Ma) might be formed in the syn-collisional stage while the Yuechengling granitoids (~437 Ma) in the post-collisional stage.

Crustal shortening, deep metamorphism, crustal collapse and extension should be involved in an orogenic cycle (Froidevaux and Ricard, 1987). Recently, a model of the Early Paleozoic magmatic activity in the SCB was related to the partially molten SCLM heated by upwelling asthenosphere triggered by lithospheric delamination is proposed (e.g., Yao et al., 2012; Wang et al., 2013b; Zhang et al., 2015; Jia et al., 2017). The Early Paleozoic volcanic and mafic rocks are rarely reported compared to granites in response to the synchronous Early Paleozoic orogeny (Wang et al., 2013b), which is similar with areas suspected to have undergone recent delamination that characterized by insignificant mafic magmatism (Ducea, 2011). And that may be due to the formation of extensive intra-crustal felsic magma and the thick Cambrian-Ordovician strata in the SCB, which acted as barriers against the rise of mafic magma (Xu and Xu, 2015). Moreover, the melting temperature for the basaltic magma and the calculated mantle potential temperature are both ca. 1,300°C, similar to that of a MORB (Mid Ocean Ridge Basalt)-like asthenospheric mantle (Yao et al., 2012), supporting the hypothesis that the partially molten SCLM was heated up by upwelling asthenosphere triggered by dropping of the delaminated lithosphere.

Based on previous studies and this study, the Early Paleozoic tectonic evolution process in the SCB is as follows:

- (1) From 460 to 440 Ma (Figure 11A), the SCB has undergone crustal shortening and crustal thickening, leading to a peak metamorphic pressure of >8 GPa and temperature of 835°C–878°C with a series of thrust faults developed (Yu et al., 2003; 2007; Li et al., 2010; Xia et al., 2014). The induced metamorphism caused melting of meta-sedimentary rocks in the crust and formed the parental magma after some degree of magma mixing. Subsequently, formation of the thrust faults provided magma conduits for intrusion or eruption of the parental magma, the syn-collisional igneous rocks were formed (e.g., Tanghu granites, Zhang et al., 2012, and the Damingshan volcanoclastic rocks in this study).
- (2) From 440 to 400 Ma (Figure 11B), the orogen gradually transforms from compression to extension. After peak metamorphism and exhumation, the extension led the metamorphism to an isothermal metamorphic temperature and decreasing pressure of ca. 4 GPa (Li et al., 2010). Due to the decreasing metamorphic pressure, the SCLM have undergone delamination with rapid unroofing and collapsing, and leading to upwelling of the asthenosphere, which input thermal for partial melting of the SCLM above (Li et al., 2010; Yao et al., 2012; Wang et al., 2013b; Xia et al., 2014). The basaltic magma formed by the partially molten SCLM underplated the crust (e.g., Jia et al., 2017), causing partial melting of the meta-sedimentary rocks to form the felsic magma. At this stage, parental magmas of some granites were formed in the interaction of the basaltic and felsic magma (e.g., Daning and Guiling granites, Tang et al., 2021). After undergoing some degree of assimilation fractional crystallization, the post-collision igneous rocks were produced

(the Yuechengling granitoids in this study). Accompanied by cooling retrogression, the orogen gradually adjusted to the normal crustal thickness, and the Early Paleozoic orogeny ended in the Early Devonian (ca. 400–390 Ma).

## 6 Conclusion

- (1) The Yuechengling granitoids (438–436 Ma) are S-type granitoids. Their parental magma was derived from a crustal meta-greywacke and meta-pelite components in the Paleoproterozoic basement, and have undergone some degree of fractional crystallization.
- (2) The Damingshan volcanoclastic rocks (later than 451 Ma) are classified as strongly peraluminous, calc-alkaline to high-K calc-alkaline volcanoclastic rocks. Their parental magma was derived from Neoproterozoic-Neoproterozoic crustal materials, and has undergone some degree of magma mixing with mantle-derived magma. The felsic parental magma was erupted to the surface in a Late Ordovician volcanic event (later than 451 Ma) and deposited soon after the eruption.
- (3) Combining with the previous studies and our new evidence on the Early Paleozoic igneous rock in the SCB, we suggest that the Early Paleozoic tectonic setting of the SCB was intracontinental orogeny rather than oceanic subduction-collision. Granitoids and volcanoclastic rocks in this study recorded the transitional stage of syn-collision compressional (ca. 460–440 Ma) and the post-collision extensional setting (ca. 440–400 Ma) of the Early Paleozoic orogeny.

## Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

## Author contributions

YT: writing-original draft, methodology. YS: supervision, conceptualization, reviewing, and editing manuscript. BW, YZ, and YL: experiment assistance, data curation. All authors contributed to the article and approved the submitted version.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2023.1202477/full#supplementary-material>

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